TREATMENT OF SEWAGE SLUDGE

This invention relates to a method of treating sewage sludge and to a sludge treated by the aforesaid method.

The treatment of raw sewage generally includes a filtration stage (in which large solids and grit are removed) followed by a stage in which the aqueous phase is subjected to aerobic bacterial action to remove biodegradable substances. This latter stage involves "activated sludge" which is essentially a concentrated bacterial mass. Biodegradable substances need to be removed prior to the discharge of the aqueous phase into watercourses, e.g. rivers, otherwise the bacterial degradation of such substances in the river would consume dissolved oxygen resulting in fish deaths, odours and general degradation of the environment. During the degradation of the biodegradable substances, growth and multiplication of the bacteria occur, resulting in the accumulation of bacterial sludge requiring disposal.

Optionally, the excess sludge may be "digested" under anaerobic conditions where, essentially, the bacteria re-equilibrate under the new conditions to produce methane and reduce the biomass but, ultimately, there remains an irreducible mass of excess sludge which requires disposal. There are a number of methods of disposal, such as landfill and disposal at sea, both of which are disfavoured for environmental reasons. Alternatively, the excess sludge may be incinerated (expensive) or spread on to agricultural land and, in the latter case, the sludge can be used as a fertiliser/soil conditioner, which is a benefit.

Unfortunately, such sludge can contain significant concentrations of pathogens and, if so, the sludge requires disinfection to reduce to an acceptable environmental and sanitary level any pathogenic organisms

present, before the disinfected sludge is spread to land. An indicator organism, used to quantify the pathogenic risk, is *E. coli*. For compliance with UK statutory provisions, for conventional treated sludge the level of *E. coli* in the sludge must be reduced by 99% (i.e. a logarithmic reduction of 2) and the maximum acceptable level of *E. coli* in the treated sewage sludge is 10^5 per gram of dry sludge (gds). For enhanced treated sludge in the UK there should be no *Salmonella spp* present and the level of *E. coli* must be reduced by at least 99.9999% (i.e. a logarithmic reduction of 6). The maximum acceptable level of *E. coli* in the enhanced treated sewage sludge is 10^3 per gram of dry sludge. Similar statutory requirements are expected to be adopted across Europe and in the USA in the future.

Bacterial reduction may be accomplished in a variety of ways including lime treatment (messy, requires significant capital investment and poses severe handling problems) heat treatment (very expensive) or merely leaving the sludge in storage till the bacterial level falls within the required limit. For the latter situation, the very large volumes of sludge involved at most sewage treatment works cannot usually be stored for the requisite time due to insufficient storage capacity. Installing sufficient capacity is either impractical due to space considerations or involves large capital expenditure.

In theory, an alternative method of reducing the bacterial content of the sludge would be to apply a disinfectant. However, disinfectants evaluated hitherto have been found to take relatively long periods to reduce the bacterial content to an acceptable level, thus creating storage demands beyond the resources of most sewage-treatment works.

We have found that the use of a phosphorus-containing compound (especially a phosphonium salt) on sewage sludge can bring about a

reduction in the pathogen content of the sludge equivalent to a logarithmic decrease of at least 2.

Accordingly, the present invention provides a method of treating sewage sludge to reduce the pathogen content of said sludge, the method comprising the steps of:

(a) adding to the sludge an effective amount of a phosphorus-containing compound; and

(b) keeping the phosphorus-containing compound in contact with the sludge for sufficient time to reduce the amount of pathogens present in the sludge by an amount equivalent to a logarithmic reduction of 2 or more.

In one embodiment the log reduction of 2 or more is achieved over a 24-hour period.

Preferably, the phosphorus-containing compound is kept in contact with the sludge for sufficient time to reduce the amount of pathogens present in the sludge by a log reduction of 3 or more and more preferably 4 or more.

The pathogens may be bacteria.

Preferably, the sludge has undergone anaerobic digestion, a process known to those skilled in the art, prior to step (a).

Preferably, the phosphorus-containing compound is a phosphonium compound, especially a tetrakis(hydroxyorgano)phosphonium salt or compound of formula (I)

$$[R'R''(CH_2OH)_2\,P^+]_n \quad X^- \quad (I)$$

wherein:

n is the valency of X;

R' and R'', which may be the same or different, are selected from an alkyl, hydroxyalkyl, alkenyl or aryl moiety and X is an anion.

R' and R'' are preferably between 1 and 20 carbon atoms in length.

X is preferably selected from the group consisting of chloride, sulphate, phosphate, acetate, oxalate and bromide.

Most preferably, the phosphonium compound is tetrakis(hydroxymethyl) phosphonium sulphate.

Alternatively, the phosphonium compound may be, for example, a tetrakis(hydroxymethyl) phosphonium chloride, tetrakis(hydroxymethyl) phosphonium bromide, tetrakis(hydroxymethyl)phosphonium phosphate, tetrakis(hydroxymethyl)phosphonium acetate or tetrakis(hydroxymethyl)phosphonium oxalate.

Alternatively, the phosphorus-containing compound may be an alkyl-substituted phosphine, e.g. tris(hydroxymethyl) phosphine as shown in formula (II):

$$(CH_2OH\,R_2)\,P \quad (II)$$

wherein:

each R, which may be the same or different, is selected from a alkyl, hydroxyalkyl, alkenyl or aryl moiety.

The amount of phosphorus-containing compound to be added to the sludge in step (a) of the method of the present invention is suitably up to 10000mg/l, preferably 100-2500mg/l, and especially 200-1000mg/l.

Alternatively, the amount of phosphorus-containing compound to be added to the sludge may be expressed relative to dry solids weight. Suitably, the amount to be added is up to about 30% by weight of dry solids. Preferably, the amount of phosphorus-containing compound to be added may be from 0.1 to 20%, for example, 0.1 to 10%, such as 0.2 to 5% or 0.4 to 2% by weight of dry solids.

Step (b) of the method of the present invention may be carried out over a period of from 1 second to 14 days. For example, from 6 to 24 hours, from 1 to 6 hours, from 1 to 60 minutes, from 1 to 60 seconds or from 1 to 15 seconds.

The rate of addition of the phosphorus-containing compound and the rate of mixing are important in maximising the efficacy of the process. To maximise efficacy, both should be as short as practically possible and contact time should be maximised. In processes involving natural gravity settling of the sewage sludge step (b) is preferably 6 to 24 hours. In processes where the treated sludge is, optionally, dewatered by, e.g. centrifuge or filter press, to produce 'sludge cake', step (b) is preferably carried out in 15 seconds to 24 hours. 'Sludge cake' has substantially higher solids content than liquid sludge. Dewatering aids such as polydiallyl-dimethyl ammonium chlorides, polyamines, cationised polyacrylamides and anionic polyacrylamides may be utilised in the production of 'sludge cake'.

The pathogens present in the sludge are suitably selected from the group consisting of:

- bacteria, including *Escherichia coli, Salmonella spp., Shigella spp., Vibrio cholerae, Bacillus cereus, Listeria monocytogenes, Campylobacter spp* and *Yersinia pestis*;
- viruses, including rotaviruses, calciviruses, group F adenoviruses and astroviruses;
- protozoans, including *Entamoeba spp., Giardia spp., Balantidium coli* and *Cryptosporidium spp.*; and
- helminths and their eggs, including nematodes, for example, *Ascaris lumbricoides* (roundworm), *Trichuris trichiura* (whipworm), *Ancylostoma duodenale* (hookworm), *Strongyloides stercoralis* (threadworm); trematodes, for example, *Schistosoma spp.*; and cestodes, for example, *Taenia saginata* (beef tapeworm) and *Taenia solum* (pork tapeworm).

Preferably the method according to the present invention provides from a two to six log reduction of the pathogens present in the sludge.

A two-log reduction is defined by 99% of the pathogens present in the sludge being eliminated. Sludge treated in this way is termed 'conventionally treated sludge'. A six-log reduction is defined by 99.9999% of the pathogens present in the sludge being eliminated. Sludge treated in this way is termed 'enhanced treated sludge'.

The present invention further provides a sewage sludge that has been treated according to the method described hereinabove.

The present invention will be illustrated by way of the following Examples.

In the Examples, the phosphorus-containing compound used to treat sewage sludge was 75% w/w tetrakis(hydroxymethyl) phosphonium sulphate, available from Rhodia Consumer Specialties Limited. For the purposes of this patent specification, the product will be subsequently referred to as "Phosphonium Salt".

As a comparison, sewage sludges were treated with a conventional disinfectant compound, dibromo-nitrilo-propionamide (DBNPA).

In each Example, the bacterium being observed was *E. coli*.

1.1 METHODOLOGY

The methodology adopted to evaluate biocide performance was by Quantitative Suspension Test (QST) using sterile anaerobic digester sludge as the QST medium, back-inoculated with *E. coli* cultures previously isolated from the sludge. In this way, a consistent chemical environment (sterile sludge) could be used in conjunction with a defined bacterial challenge. This enables the provision of consistency between tests.

1.2 MICROBIOLOGICAL EVALUATIONS

Sterile sludge was prepared from raw sludge samples by autoclaving at 121°C for 20 minutes. The *E. coli* strains used in QST had been isolated from raw sludge samples.

QST were performed as follows:

- Sterile sludge (19ml) was dispensed into sterile, screw-cap, plastics universal bottles of nominal 30ml capacity.

- To each sample was added 0.5ml of a washed cell suspension of *E. coli* prepared from a 16-hour culture incubated at 44°C in Tryptose Soy Broth, which had been centrifuged (14500 rpm for 10 min.) and re-suspended in sterile phosphate buffer (0.2M at pH 7.2). An inoculum of 0.5ml was sufficient to provide a final cell concentration of about 10^8 per ml in 20 ml of QST medium.

- Fresh stock solutions of the candidate treatment chemicals were prepared in sterile phosphate buffer (0.2M at pH 7.2) at concentrations such that when 0.5ml was added to the QST medium (final volume 20ml) the desired final concentration of biocide was achieved.

- The QST medium was mixed thoroughly and held at 22°C for the duration of the test.

- At intervals during the test, the sludge was well mixed and samples (1.0ml) were removed from the QST medium and inoculated into the first tube of a dilution series containing MacConkey broth supplemented with sodium thiosulphate (5.0 g/l), to inactivate any residual biocide carried into the dilution series. This was carried out in duplicate.

- The remainder of the serial dilution (10 fold steps) was carried out in MacConkey Broth alone and tubes incubated at 44°C for 16 hours. The end point was scored as the highest dilution in the series to show a change in colour from purple to yellow and to have developed turbidity.

MacConkey Broth was selected as this medium contains the pH indicator Bromocresol Purple that changes from purple to yellow as the medium becomes acidic. This is a useful indirect indicator of microbial growth (organic acid production) where this cannot be scored by the development of turbidity in an initially clear medium. Because the sludge contains suspended solids the first 2 tubes of the dilution series instantaneously develop turbidity on the addition of the sludge. This precludes using turbidity alone as an indicator of microbial growth.

The biocides used in the evaluations are shown in the Table below.

BIOCIDE TYPE	ACTIVE INGREDIENT (ai)	PERCENT ai
Phosphonium Salt	THPS	75
DBNPA	DBNPA	98

EXAMPLES 1 to 3

The performance of Phosphonium Salt in the concentration range 250 to 1000mg/l is illustrated in Figure 1 of the accompanying drawings. Concentrations of 250 and 500 mg/l gave similar results with a fairly flat time/kill response over the first 6 hours contact time, followed by a reduction in numbers to a total kill within 48 hours.

By contrast, the time/kill response at 1000mg/l was much faster. The time/kill response over the first 6 hours contact time was more progressive and total kill was achieved within 24 hours.

For comparison, the *E. coli* levels in untreated sludge slowly decrease naturally, over a time period as shown in figure 2. Even starting at the low *E. coli* level of 10^4 cfu/gds it took 6 days to achieve total kill. Starting at the higher level of $10^{8.5}$ cfu/gds, the level had only reduced to

10^4 cfu/gds after 8days. The benefit of phosphonium salt treatment (figure 1) is therefore effectively displayed.

EXAMPLE 4

The performance of Phosphonium Salt compared to that of DBNPA, is shown in Figure 3 of the accompanying drawings. Both biocides were tested at an equal active-ingredient concentration of 500mg/l. DBNPA shows surprisingly poor anti-microbial performance, achieving only a 2.5 log reduction in numbers after 48 hours.

The foregoing Examples demonstrate the following characteristics of the present invention:

(a) Increasing the Phosphonium Salt concentration used in treatment from 500 to 1000mg/l gives a significant improvement in performance.

(b) In all of the treatments evaluated total kill was achieved.

(c) When compared with the performance of DBNPA, the performance of Phosphonium Salt was superior.